Lothar Schafer
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University of Arkansas
Fayetteville, Arkansas 72701

To
Dr. Spiro G. Lekoudis, Code 1132
Director, Mechanics Division
Department of the NAVY
Office Of The Chief of Naval Research
Arlington, Virginia 22217-5000

September 10, 1991

Reference: 5000
Ser 1132/116

Attention Mrs. Michelle D. Parker

Dear Dr. Lekoudis:

In accordance with the general instructions, I am mailing to you our final yearly summary of research performed under our ONR research contract for the Mechanics Division.

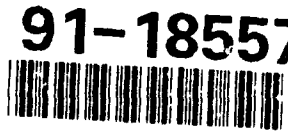
Two copies of this "End-of-the-fiscal-year" letter are enclosed. I hope that you will find the material satisfactory and thank you very much for your support.

Sincerely,

Lothar Schafer

Lothar Schafer
E. Wertheim Professor of Chemistry

cc: Martial W. Davoust, Administrative Contracting Officer (1 copy)
Director, Naval Research Laboratory (6 copies)
Defense Technical Information Center (12 copies)



OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
1 October 1990 through 30 September 1991

R&T Number: 4132H804

Contract/Grant Title: Time-Resolved Electron Diffraction Studies...

Scientific Officer: R.S.Miller

Principal Investigator: Lothar Schafer

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Fayetteville, AR 72701

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a. Number of Papers Submitted to Referred Journal but not yet published: (work finished on two which are in prep.) one accepted;

b. Number of Papers Published in Referred Journals: (List Attached): ---

c. Number of Books or Chapters Submitted but not yet Published: ---

d. Number of Books or Chapters Published (List Attached): ---

e. Number of Printed Technical Reports & Non-Referred Papers (List Attached): ---

f. Number of Patents Filed: ---

g. Number of Patents Granted (List Attached): ---

h. Number of Invited Presentations at Workshops or Professional Society Meeting (List Attached): two
also: two invitations by private corporations; five by Universities in US and EUR.

i. Number of Presentations at Workshops or Professional Society Meetings (List Attached): ---

j. Honors/Awards/Prizes for Contract/Grant Employees: (List Attached, may include Society Awards/Offices, Promotions, Faculty Awards/Offices, etc.) ---

k. Providing the following information will assist with statistical purposes.

PI/CO-PI:	TOTAL	three	Grad Students:**	TOTAL	two
	Female	---		Female	one
	Minority*	---		Minority*	---

Post Doc:**	TOTAL	one
	Female	---
	Minority*	---

Also: Two Undergrad Students;
One female.

1. Degrees Granted (List Attached): ---

* Underrepresented or minority groups include Blacks, Hispanics, and Native Americans.
Asians are not considered an underrepresented or minority group in science and engineering.

** Supported at least 25% this year on contract/grant.

Statement A per telecon Dr Richard Miller
ONR/Code 1132
Arlington, VA 22217-5000

NWW 2/10/92

Enclosure(1)

a. Description of Scientific Research Goals.

It is the goal of this research to perform gas electron diffraction (GED) studies, time-resolved and not time-resolved, of the photochemical and thermal decomposition of RDX and trinitro-azetidine. (Proposal 7MAR88 to 15AUG90; no-cost extension granted to 15AUG91.) The two compounds are highly explosive. Therefore, the GED experiments are not routine and feasibility of the project had to be demonstrated first by recording the groundstate data of the two systems. Two specific problems were identified and discussed in the original proposal:

1.) Can effective vapor densities of RDX or TNAZ be achieved which are sufficient for GED studies?
2.) After flash heating or laser excitation, can important intermediates of decomposition be identified in the product mixtures?

In last year's report we described the successful completion of part 1: groundstate GED data of RDX and TNAZ, and thermal decomposition data of TNAZ were recorded. Concomitant with these activities and in support of the GED data analyses, ab initio geometry optimizations of the various groundstate conformations of RDX and TNAZ were executed to make possible MOCED (Molecular Orbital Constrained Electron Diffraction) studies as described in the proposal.

Part 2 of the research plan identified above entailed continued construction of a pulsed electron beam apparatus for time-resolved electron diffraction (TRED) studies of RDX and TNAZ. With the limited resources available to us during the no-cost extension period of the grant, we concentrated on this aspect of our research.

b. Significant Results of the Recent Past.

TRED Instrumentation Development.

The time-resolved electron diffraction apparatus is of particular significance for the proposed project. In previous years, we were able to implement the proposed photocathode to generate a pulsed electron beam; then we succeeded in recording electron diffraction data of polycrystalline materials on the TRED instrument in real-time (intensities of polycrystalline gold were included in our last report); and last our efforts were focused on preparing the instrument for the recording of gas phase data.

Last year we were able to report that all instrument modifications needed for gas phase work had been implemented and that, for the first time it was possible to record gas phase data of some test molecules, such as SF_6 and CCl_4, in their ground states. However, the quality of these data was not good enough to publish a report on our results. The apparatus did not work consistently, its performance was borderline, and experiments could not be repeated as desired.

Several problems were identified that had to be solved to improve the performance of the TRED instrument to the extent that intensities can be recorded from laser excited RDX and TNAZ. In response to these analyses, the electron beam intensity was stabilized by reconstructing the photocathode. Its titanium surface was replaced by tantalum for the reasons described in the last report, and a high capacity charge storage device was included in the gun to avoid an unacceptable voltage drop during pulse emission.

Hundreds of experiments were performed during the last year to discover the effective procedures for beam adjustment and general fine tuning of all components. The experiment is highly complex, a large number of interrelated and delicate components (two excimer lasers, the high voltage photocathode, the optical and electron beam tracks, synchronization circuitry, the vacuum environment, photodiode array detection and signal processing) had to be coordinated perfectly to yield useful results.

The last weeks of the grant brought a decisive success. We were able to refine the most important operational parameters of the TRED instrument to such an extent that we can now obtain electron diffaction intensities of laser irradiated gases consistently and with reproducible results.

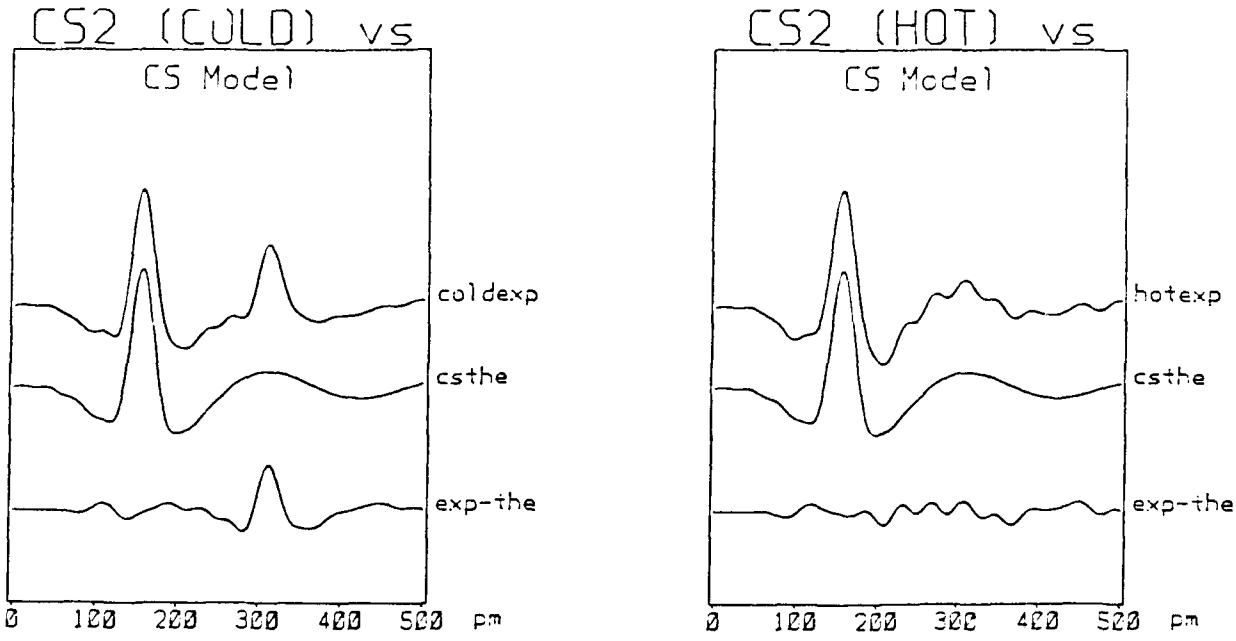

Figure 1

Gas electron diffraction experiments with laser excited carbon disulfide.

Figure on the left shows the experimental radial distribution curve of CS_2 obtained with our pulsed electron beam apparatus and real-time data recording. The peaks in the experimental curve (coldexp) correspond to the C=S bond (in the vicinity of 150 pm), and to the non-bonded S...S distance (in the vicinity of 300 pm). Since inner data are missing, the zero line is curved. The theoretical curve (csthe) is for carbon monosulfide. The zero line is also curved since inner data were not included in the Fourier transform, but the S...S peak is clearly missing. The difference experiment minus theory, is given at the bottom of the Figure. It shows the absence of S...S in C≡S theory.

Figure on the right shows the experimental radial distribution curve of laser irradiated CS_2. The difference curve, experiment minus C≡S theory, shows that there is no S...S peak in the laser excited gas. Thus, the irradiation of CS_2 with 193 nm pulses has led to the formation of carbon monosulfide.

Experiments so far have involved test molecules which are gases at room temperature. Experiments with the solids, TNAZ and RDX, have not yet been performed since additional difficulties are involved. Nevertheless the recent results represent a true breakthrough and have brought the project within reach of the intended goal.

To illustrate the exciting experiments, never achieved before, that we can now perform in principle, but not any more in fact due to the lack of funds, in Figure 1 we show the results of a gas electron diffraction study of the 193 nm photofragmentation of carbon disulfide. The Figure shows on the left the experimental radial distribution curve for CS_2 taken without laser irradiation. The curve is characterized by two distinct peaks, the C=S bond length at 150 pm, and the S...S non-bonded distance at about 300 pm. When the laser is turned on and the scattering recorded from the excited gas, the radial distribution curve obtained shows the absence of the S...S peak, and a single C≡S bond distance.

Diffraction intensities on which these curves are based are still noisier than typical intensities recorded with conventional means, and the data range s=3/Å to 18/Å is relatively short. Nevertheless, the 193 nm photofragmentation of CS_2 to C≡S is clearly demonstrated. The same results were obtained consistently in a series of repeated experiments.

Many unsuccessful attempts have been reported in the literature of recording gas electron diffraction intensities, with or without pulsed electron beams, of unstable molecular systems. The data shown in Figure 1, of a highly reactive species, carbon monosulfide, document the first successful pump-and-probe pulsed-beam gas phase electron diffraction experiment that has yielded quantitatively accurate data for a photogenerated reactive molecular state.

c. Plans for next year's research.

The grant ended with the end of the extended grant period, 15AUG91. There are no other funds to continue this project.

During the last decade we have been able to establish the world's leading laboratory in modern gas electron diffraction. It is with considerable regret that we are now terminating the research outlined above.

List of Publications/Reports/Presentations

1. Project Related Publications in Refereed Journals (in press and in preparation):

1. R. Bakhtiar, J. Coffin, S. Q. Newton, K. Siam, J. D.Ewbank, and L. Schafer, "Molecular Structure of Trinitroazetidine by Gas Electron Diffraction and Ab Initio Calculations", J. Mol. Struct., to be submitted.

2. J. Coffin, S.Q. Newton, K. Siam, J. D. Ewbank, C. van Alsenoy and L. Schafer, "Ab Initio Geometry Determination and Conformational Analysis of RDX", J. Mol. Struct., in press.

3. J.D. Ewbank, W.L. Faust, J.Y. Luo, J. English, D.L. Monts, Q. Dou, D.W. Paul, and L. Schafer, "A Pulsed-Beam Gas Electron Diffraction Study of the 193 nm Photofragmentation of CS_2", to be submitted.

2. Books (and sections) Published: none

3. Technical Reports: none.

4. Presentations concerning the research program of the group.
a.Invited:

L. Schafer, University of Kansas, Fall 1990

L. Schafer, Se-Sw Regional ACS Meeting, Symposium Lecture, University of New Orleans, Fall 1990

L. Schafer, Merck Pharmaceutical Corporation. Rahway, N. J., Fall 1990

L. Schafer, Workshop on Parameter Development, Polygen Corp., Waltham MA, Spring 1991

L. Schafer, University of Duisburg, Germany, May 91.

L. Schafer, University of Marburg, Germany, May 91.

L. Schafer, University of Wuppertal, Germany, May 91.

L. Schafer, University of Nancy, France, May 91.

L. Schafer, Hoechst Corp., Frankfurt, Germany, May 91.

5. Patents Granted: none.

6. Degrees Granted: none.

LIST OF AWARDS

Name of Person Receiving Award.	Institution	Name of Award	Sponsor

none.

h. List of Participants.

At the University of Arkansas:

1. Dr. John D. Ewbank, Associate Professor, PhD 1974, U of Arkansas.
2. Dr. David W. Paul, Associate Professor, PhD 1981, U of Cincinnati.
3. Dr. Lothar Schafer, Distinguished Professor, PhD 1965, U of Munich.
4. Dr. Jing Yuan Luo, Visiting Research Instructor, from East China University of Chemical Technology, Shanghai, China.
5. Susan Kulp, graduate student.
6. Jeff English, graduate student.
7. Alastair Jones, Research Experience for Undergraduates Participant, from Sussex University, England.
8. Tamara Harris, Research Experience for Undergraduates Participant, from Southwest Baptist University, Missouri.

At NRL:

Dr. W. L. Faust, Optics Division.

OTHER SPONSORED RESEARCH

J.D. Ewbank, D.W. Paul, and L.Schafer, "Research Toward the Application of Real-Time Gas Electron Diffraction as a Detector for Gas Chromatography", NSF, $161520, 1JAN91 to 30JUN93.